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Engineering surface roughness of nanocellulose film via spraying to produce smooth substrates

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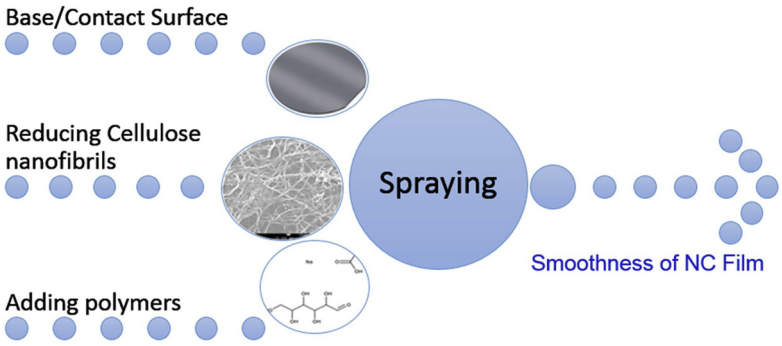
GRAPHICAL ABSTRACT



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ABSTRACT

Due to the requirements of smooth cellulose substrates for printing electronic circuits to have proper conductance, nanocellulose (NC) have been used as a substrate for electronic material such as solar panels, supercapacitors and flexible electronics etc. Recently we developed a process to produce smooth NC films by spraying onto an impermeable substrate. The spray coated NC film has a shiny and glossy smooth surface where it was in contact with the substrate. In this study, we investigated the effect of i) substrate surface chemistry, ii) substrate roughness, iii) NC fibre diameter and iv) addition of carboxymethyl cellulose (CMC) in NC suspension on the roughness of the smooth surface of NC film. The three parameters controlling the roughness of the resultant NC films were the roughness of the substrate surface, the fibril diameter of the NC and CMC addition.

Adding 1.5 wt. % CMC had only a small effect with very smooth substrates but had a larger effect with rougher substrates. The best roughness obtained is 336 ± 117 nm at a 259.1 μm × 259.9 μm inspection area when spraying of 1.5 wt. % CMC – 1.75 wt.% NC suspension on the super polished stainless steel (SSS). The controlling order of roughness of NC films was found to be 1.5 wt. % CMC addition in 1.75 wt.% NC suspension > base substrate > fibril diameter. The addition of CMC in the film decreases the surface roughness by

Abbreviations: NC, nanocellulose; RFID, radiofrequency identification device; OLED, organic light emitting diode; PV, photovoltaic cells; MFC, micro fibrillated cellulose; RMS, root mean square; NFC, Nano fibrillated cellulose; OSSS, ordinary stainless-steel plate; OSSC, ordinary stainless-steel circular; SSS, super mirror stainless steel plate; SW, silicon wafer; CMC, carboxymethyl cellulose; AFM, atomic force microscopy

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reducing the friction experienced between the fibres. This reduction in friction allows the fibril network to form a smoother film when compared to a film without the presence of CMC.

This study has shown that spraying of NC on base surfaces produce a smooth NC film in a rapid single step, with a smoothness that can be tailored across fibrils.

1. Introduction

Developing an eco-friendly substrate from natural polymers is one of the requirements of biodegradable substrates for designing flexible electronic devices. The smoothness of the substrate controls the conductive ink spreading on the surface and avoids forming discontinuities within the ink once on the substrate. Synthetic plastics can also be used as base substrates for printed electronics, however, these are not biodegradable, and require surface treatment to achieve a suitable smoothness. Moreover, the increased awareness of sustainability and environmental issues among people has driven researchers towards the replacement and reduction of the use of plastic materials [1]. Paper can be used as a low-cost substrate for fabricating electronic materials and offers the advantage of removing the plastic-based components from the current devices. However, paper substrates are susceptible to moisture absorption, have a high surface roughness and can be highly porous, which limits their use in high-performance electronic materials [2].

Nanocellulose (NC) can be used as a sustainable and eco-friendly substrate in the fabrication of printed electronics [3] and when mixed with inorganic fillers, it could control and reduce the surface roughness [4]. NC has a high aspect ratio, with the fibre diameter ranging from 20 nm to 100 nm and length to a few micrometres. NC has high strength and the ability to form a compact network with considerable resistance to air, oxygen and water vapour permeance [5]. Due to the good barrier performance of NC, it could be a potential substrate with a suitable roughness for printing electronic circuits.

The surface roughness of an NC film determines its glossy appearance as a finishing quality of the film. Lowest roughness NC films could replace synthetic plastics as base substrates for printing circuits. The main laboratory applications of smooth NC films investigated are its use in the fabrication of Radiofrequency Identification device (RFID) tags, Organic Light Emitting Diode OLEDs, photovoltaic (PV) cells, electronic paper, cellulose-based batteries [6], membranes for water filtration [7], substrate for biosensors, diagnostics and bioactive interfaces [8].

The printing process in the construction of printed electronics is highly dependent on the surface roughness of the substrate [6]. If a substrate has a high surface roughness, the quality and precision of the printed ink layer will decrease. This is due to various phenomena such as wetting and adhesion of ink layer on the substrates. The dried ink layers influence the performance of printed electronics devices. As surface smoothness and surface energy are interlinked, they play a contributing role in the performance of the ink layer on the substrates. Accordingly, the reduction of surface roughness leads to higher performance printed electronic devices.

Vacuum filtration is a conventional method for preparing NC films [9]. The surface of mesh in the vacuum filtration produces a film with considerable roughness and also transfers filter marks to the film which results in high roughness on both sides [10]. In comparison, casting is a laboratory method for preparing NC films and the roughness of the NC film produced via this method depends on the fibre size and surface of the base material. However, this method is limited to laboratory scale production of NC films [11]. Time consumption for fabricating NC film by casting varied from days to weeks.

Calendering is a conventional process of smoothening cellulose macrofibre materials such as paper sheets with the compression of fibres with heated rolls. The cellulose sheet produced via this process is smooth and glossy. This is a final step in the industrial finishing of paper that could reduce the surface roughness [12] and porosity of the sheet. Calendering was implemented to smooth the surface of micro fibrillated cellulose (MFC) filler composites for flexible electronics applications. The mean surface roughness of the calendered MFC films varied from 470 nm to 341 nm at an inspection length of 30 mm in the film and has achieved a surface smoothness lower than that of a photo paper [4]. Whilst, calendering is a high temperature technique that produces sheets, which have a smoother surface, the other properties of sheets such as thickness, strength and stiffness are compromised.

Recently, we developed a new method of spraying of nanocellulose on polished stainless-steel surfaces to produce smooth nanocellulose films. The measured RMS roughnesses were 389 nm and 81.1 nm at an inspection area of 94 μm × 125μm from optical profilometry and 10 μm × 10 μm for AFM evaluation [10]. These values confirm spray coating as an appropriate method to engineer the roughness of NC films. It is flexible in the processing of NC film and film uniformity and properties can be controlled by suspension concentration and process variables in spraying [13].

This paper investigates the factors that control the roughness of NC films prepared by spraying. This includes the study of the effect of substrate roughness, NC fibre diameter and the addition of a water-soluble polymer to reduce the fibre-fibre friction during film formation. This will be a platform for the production of NC films with controlled smoothness for specific high-performance applications.

2. Materials and methods

2.1. Preparation of nanocellulose (NC) suspension

The nomenclature for nanocellulose has not been reported consistently within the literature. It has been called microfibrillated cellulose (MFC), cellulose nano-fibrils, cellulose micro-fibrils and nanofibrillated cellulose (NFC). In this paper, we use NC as the generic term for the cellulose nanomaterials used. The NC used was supplied from DAICEL Chemical Industries Limited (Celish KY-100S) at 25 wt. % solids content. This NC has cellulose fibrils with an average diameter of approximately 73 nm with a wide distribution of fibre diameter, and an average aspect ratio of 142 ± 28 [14]. NC suspension was prepared by diluting the original concentration of 25 wt. % to 1.75 wt. % NC suspension with de-ionized water and disintegrating for 15,000 revolutions at 3000 rpm in a disintegrator.

2.2. Selection of base substrates

The base substrates used for tuning the roughness of the nanocellulose films were ordinary stainless-steel plate (OSSS) (220 mm × 220 mm), ordinary stainless-steel circular (OSSC) (159 mm diameter), super mirror stainless steel plate (SSS) (220 mm × 220 mm) and silicon wafer (SW) (152.4 mm diameter). The surface of OSSS contains many scratches and lines which elevates the roughness. The OSSC has more refined polishing than OSSS and therefore, a lower surface roughness. The silicon wafer is GAS06 -Size 6 " Silicon Wafer, Type P, 111 (Boron–1 primary flat) with a resistance of 1–30 Ohms from Pro Science Technology Central Queensland Australia. The silicon wafer has been polished with one side having a roughness of 2 A°. The thickness of this 6-inch wafer varies from 600 ± 20–690 ± 20 μm. The super mirror polished stainless steel from Rimex Metals (Australia) Pty Ltd, Somersby, NSW 2250, Australia, is 316 grade and it is surface mechanical polished to a mirror glass standard, with surface reflectivity of greater than 90 %.

The surface roughness of these substrates is given in Table 1 and their surface images are shown in Figure S3 in supplementary information.

2.3. Preparation of smooth NC films via spraying

The experimental set-up for a bench scale spray coating system with experimental conditions is shown in Fig. 1. The NC spray coated film is prepared according to the reported method [13] by spraying onto a base surface of interest, which has been placed on a moving conveyor at a fixed velocity 1.25 ± 0.15 cm/sec. The NC suspension was sprayed using a Professional Wagner spray system (Model number 117) at a pressure of 100 bar. The type 317 spray tip used in the spray system produced an elliptical spray jet and the spray jet angle and beam width are 50° and 22.5 cm, respectively. The spray distance is 50.0 ± 1.0 cm from the spray nozzle to the base substrate. Prior to the spraying of NC on the substrates, the pressure driven spray system was run for sufficient time to allow the system to reach equilibrium. After spraying, the film on the plate was dried under standard laboratory conditions for at least 24 h. The dried NC film was readily peeled from all substrates.

2.4. Tuning roughness of NC films

The following variables were investigated:

1 Varying the substrate roughness using the materials listed in Table 1.
2 Varying the cellulose nanofibril diameter via high-pressure homogenization of NC sprayed on the surfaces i) first pass with pressure of 1000 bar ii) second pass with pressure of 800 bar.
3 Adding 1.5 wt.% carboxymethyl cellulose (CMC) into 1.75 wt.% NC suspension and spraying on the substrates.

2.5. High-pressure homogenization of NC

1.75 wt. % NC suspension was fibrillated in a GEA Niro Soavi (Laboratory scale) high-pressure homogeniser and subjected to 1 or 2 passes before spraying. The number of passes that the NC suspension goes through the homogenizer controls the diameter of cellulose nanofibrils in the NC. The pressure in homogenizer was at 1000 bar in first pass and 800 bar in the second pass.

2.6. Evaluating NC fibril diameter and aspect ratio

A drop of 0.2 wt. % of homogenized NC suspension was cast on a silicon wafer and then dried in a controlled laboratory environment. The dried suspension on the silicon wafer was coated with iridium. Micrographs were taken with a FEI Magellan 400 FEG SEM using the Through Lens Detector (TLD) at a voltage of 5 keV. The micrographs were taken at a scale bar of 1 μm and magnification of 150,000 × . The diameter distribution of NC fibres was measured with Image J (1.51 K National Institute of Health (NIH) USA). The data reports an average diameter of NC with 95 % confidence interval. The diameter of NC after 1st and 2nd pass homogenization are ≈40 nm and ≈20 nm. The aspect ratio of NC fibrils was evaluated by the sedimentation method [14].

2.7. CMC addition in NC suspension

Carboxymethyl Cellulose (CMC) (Finnfix grade 10 from CP Kelco, USA) was used to prepare NC films containing CMC via spraying. To avoid the formation of agglomerates, 15 g of dry carboxy methyl cellulose (CMC) was slowly added into 915 g of distilled water whilst being agitated at 600 rpm with a mixer. The resultant solution is 930 g of suspension. To this is added 70 g of DAICEL NC (Default NC) at 25 wt. % solids content to make 1 kg of suspension with 1.75 wt. % of nanocellulose fibre in the suspension and 1.5 wt. % of CMC, for a total solids content of 3.25 wt.% NC-CMC. This suspension was disintegrated at 3000 RPM in a disintegrator for 15000 revs.

2.8. Optical profilometry

The size of specimen area from smooth NC films was 100 mm^2 selected from uniform films free from surface defects and pinholes. The NC film peeled from the substrate was the smooth surface of the NC film and the side exposed to air was the rough side. The spraying of 1.75 wt. % NC suspension on these surfaces produces a basis weight 55 g/m^2 and thickness 108.9 μm of NC film. An optical profiler (Olympus OLS 5000 Laser Confocal Microscope) was used to evaluate the aerial roughness of a 259 μm × 259 μm area of the NC films of both the rough and smooth sides. The average aerial roughness, Sa and root mean square (RMS) roughness, Sq of both sides of NC films were evaluated from the instrument software. Six films were taken for measuring the roughness parameters. A minimum six locations on each film were considered for aerial roughness evaluation.

2.9. Scanning electron microscopy of smooth NC films

The surface morphology and topography of the smooth surface of the NC film were studied with FEI Nova NanoSEM 450 FEGSEM using a TLD. The sample were coated with a thin layer of iridium metal prior to imaging. The images were captured with magnification varying from 80,000 x to 150,000 x in secondary electron mode-II of FEI Novo SEM.

3. Results

The aerial roughness parameters of NC films were evaluated from the statistical analysis of optical profiler images. The surface roughness of NC film derives from irregularities or unevenness and coarse texture produced by cellulose nanofibrils, imprints transcribed from the base substrates and also aggregates formed in the spraying process. It evaluates the vertical deviation from the actual surface through the parameters such as an average roughness (Sa) and root mean square roughness (RMS), Sq. Sa is an arithmetic mean of the height of the surface profile on the NC film [15]. Sa provides statistically stable and more accurate measurement with optical profilometry. However, it has limitations to differentiate between peaks and valleys on the surface. Sq is more sensitive to peaks and valleys than that of Sa because it is a square of height at the surface. RMS roughness Sq, provides authentic information about surface height variations on cellulose substrates and is considered as a quality indicator of the surface [16,17]. In this work, both Sa and Sq have been reported.

Table 1
Types of substrates and its surface roughness.

Types of Substrates	Average Roughness (Sa) nm	RMS Roughness Sq nm
Ordinary stainless-steel square	333 ± 38	432 ± 44
Ordinary stainless-steel circular	131 ± 23	195 ± 33
Silicon Wafer	17 ± 03	25 ± 04
Super polished stainless steel	18 ± 04	22 ± 04

*The error bars give the 95 % CI from descriptive statistics.

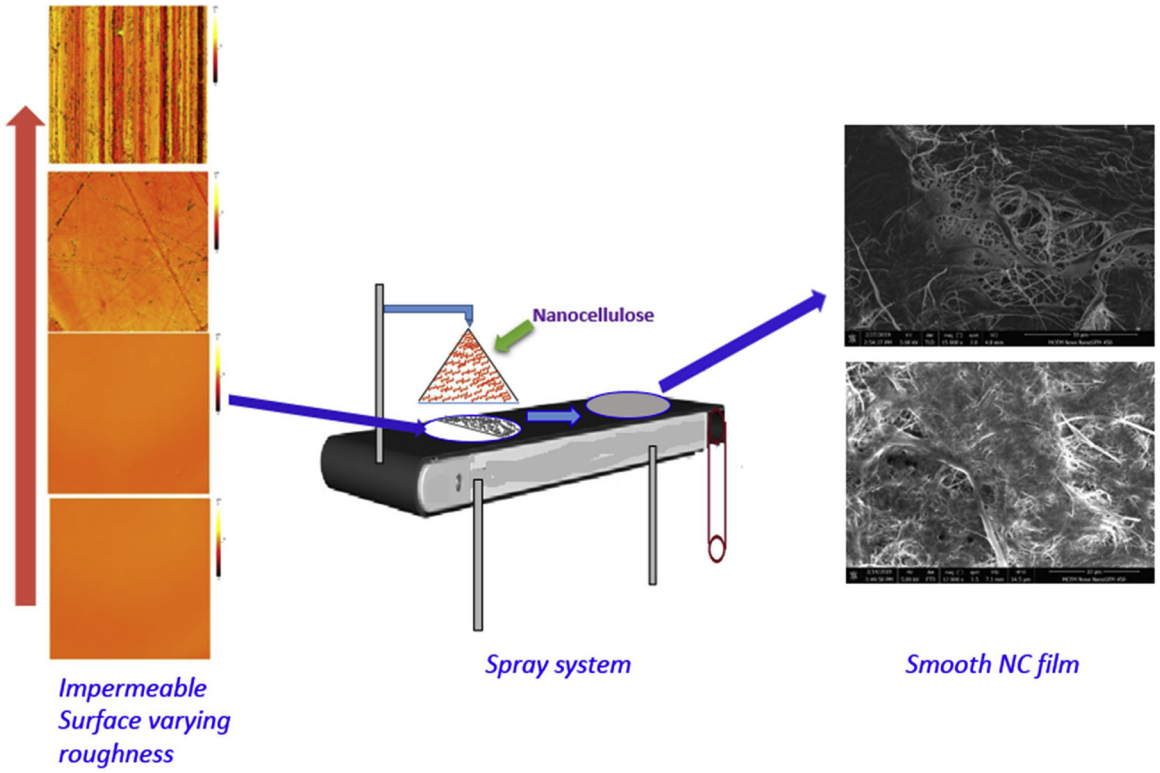

Fig. 1. Experimental Set-up for Smooth NC production. The spraying of NC on the base substrates produce smooth NC films.

The roughness of all the impermeable substrates was measured using optical profilometry at an inspection size of 259 μm × 259 μm. Table 2 lists the results on the roughness of smooth side of NC film. The OSSS and OSSC substrates show a significant difference between Sa and Sq due to presence of scratches and marks on their surfaces. This elevates the roughness of the NC film produced on OSSS via imprinting these markings on the film. When compared to OSSS, OSSC is a quite polished substrate, which yields a low film roughness. The optical profilometry images of these substrates are added in the supplementary information.

The data set in Table 2 is the average from different experiments at three different solids contents (The solid content used 1.25 wt. %, 1.75 wt. % and 2.25 wt. %), while the data in Fig. 4, gives the data obtained at 1.75 wt. % only. The high-pressure homogenization of 1.75 wt. % was performed to make films. If the suspension exceeds 2.wt. % solid content, then it is difficult to homogenise as the jelly-like nature of the suspension causes clogging.

Fig. 2 shows optical profilometry images of smooth NC film and confirms the increase in surface smoothness of NC film when spraying on smoother base substrates. Additional images of the base surface and smooth NC film from were added in Figure S1 and S2 in the supplementary information.

The SEM Micrographs of smooth NC films are shown in Fig. 3. The surface of the CMC-NC film peeled from super polished stainless steel has the lowest smoothness for printed electronics applications compared the NC film from OSSS. The smooth NC film has a compact network of compressed fibrils in the film, is less porous on the smooth side and has a glossy surface with high smoothness.

3.1. Effect of surface substrates

Fig. 4 shows the effect of the base surface on the Sa and Sq surface roughness of the NC film peeled from the different base substrates with varying roughness. The results show that the substrate roughness has a significant influence on the film roughness, but that the extrapolated roughness for spraying on an infinitely smooth substrate is not zero.

The trends of the plot between film surface roughness and base substrate roughness have two components. One was the roughness of the underlying substrate and the other is the roughness created by the packing of the fibres on that substrate. The slope of the data in the plots are 2.04 and 1.95 for RMS roughness and average roughness, respectively. The fact that these slopes are greater than 1.0 shows that there are synergistic effects between substrate roughness and fibre network induced roughness.

The peeling of NC film from the silicon wafer is quite challenging due to the strong interaction of fibres with the hydrophilic surface of the silicon wafer. Its surface is more hydrophilic than stainless steel surfaces. Therefore, since the RMS roughness of the SW was slightly higher than the SSS, the Sa of the NC film from the SW is also slightly higher than the film peeled from SSS. The correlations between the aerial surface roughness of NC film and base surface are as follows.

Table 2
Surface Roughness of Spray Coated Side of NC Film. The error bars give the 95 % confidence intervals of the mean.

Controlling Parameters	Substrates		
	OSSS	SSS	SW
Average Roughness Sa of NC film in nm			
Only Base Surface (Ave Diameter of NC ≈ 70 nm)	1055 ± 79	402 ± 23	479 ± 31
Fibre Diameter (≈ 40 nm)	1057 ± 139	443 ± 81	405 ± 36
Fibre Diameter (≈ 20 nm)	1038 ± 218	362	368 ± 32
CMC addition	396 ± 28	262 ± 26	310 ± 31
RMS Roughness, Sq of NC film in nm			
Only Base Surface	1400 ± 269	550 ± 36	610 ± 51
Fibre Diameter (≈ 40 nm)	1339 ± 167	585 ± 106	558 ± 61
Fibre Diameter (≈ 20 nm)	1318 ± 261	471 ± 20	491 ± 42
CMC addition	508 ± 34	345 ± 37	336 ± 117

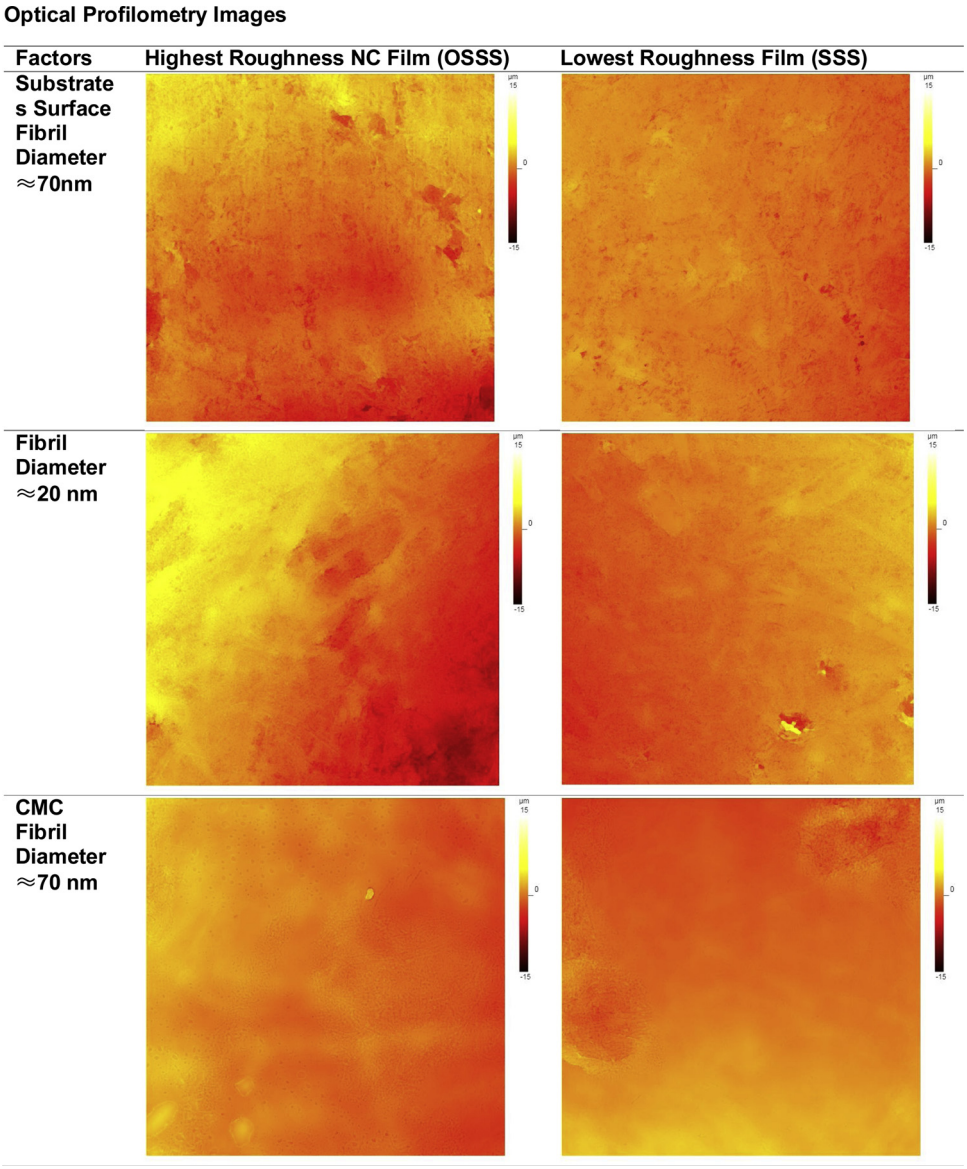

Fig. 2. Optical profilometry images of NC film (50X magnification). The inspection size of specimen is 259 μm × 259 μm. The height is shown by the colour given in the legend.

$$Sa_{film} = 426 + 1.95\,SRa_{base} \quad (1)$$

$$Sq_{film} = 562 + 2.04\,SRq_{base} \quad (2)$$

Where Sa_{film} and Sq_{film} are the average roughness and RMS of spray coated NC film with these substrates. SRa_{base} and SRq_{base} are the average roughness and RMS roughness of the base surface. The intercept of the plot indicates the minimum surface aerial roughness of spray coated NC films. The fibres in spray coated NC film have an average diameter of ≈70 nm and an aspect ratio of 142 ± 28 [18]. The minimum average surface roughness, Sa and RMS roughness, Sq of spray coated NC film are 426 nm and 562 nm.

The roughness of the free side of spray coated NC film was measured and added in the supplementary information. Moreover, the macro scale roughness of spray coated NC film is evaluated with Parker Print Surface instrument shown in Figure S7 and S8 and added in the supplementary information. This data confirms the smoothness of the NC film increased when sprayed on the solid substrates with decreasing roughness.

3.2. Effect of homogenization of NC and CMC addition

Figs. 5 and 6 show the effect of homogenization and CMC addition respectively on Sa and Sq. The two hypotheses tested are a) that the reduction of fibrils diameter and its length via high pressure homogenization will better allow the fibrils to conform to the base substrate and b) the addition of the CMC will reduce the friction between the fibrils to allow them to conform better, creating a smoother surface. The NC fibres were homogenised either for 1 or 2 passes. Single pass homogenization reduced the fibre diameter from 70 to 40 nm. The diameter was further reduced to 20 nm with 2 pass homogenization. The diameter distribution results are shown in Fig. 5.

The nanoscale average roughness (Sa) of the NC film on the base substrate varied from 465 to 362 nm with SSS, when the nanofibril diameter varied ≈70 nm to ≈20 nm. It confirms the diameter of cellulose nanofibrils as another important controlling parameter on surface roughness. The correlation of each condition has been shown in Figs. 7 and 8. Each intercept from the plot is the minimum surface roughness of NC film that could be achieved. It depends on the diameter of cellulose nanofibrils and its aspect ratio. Simultaneously, the

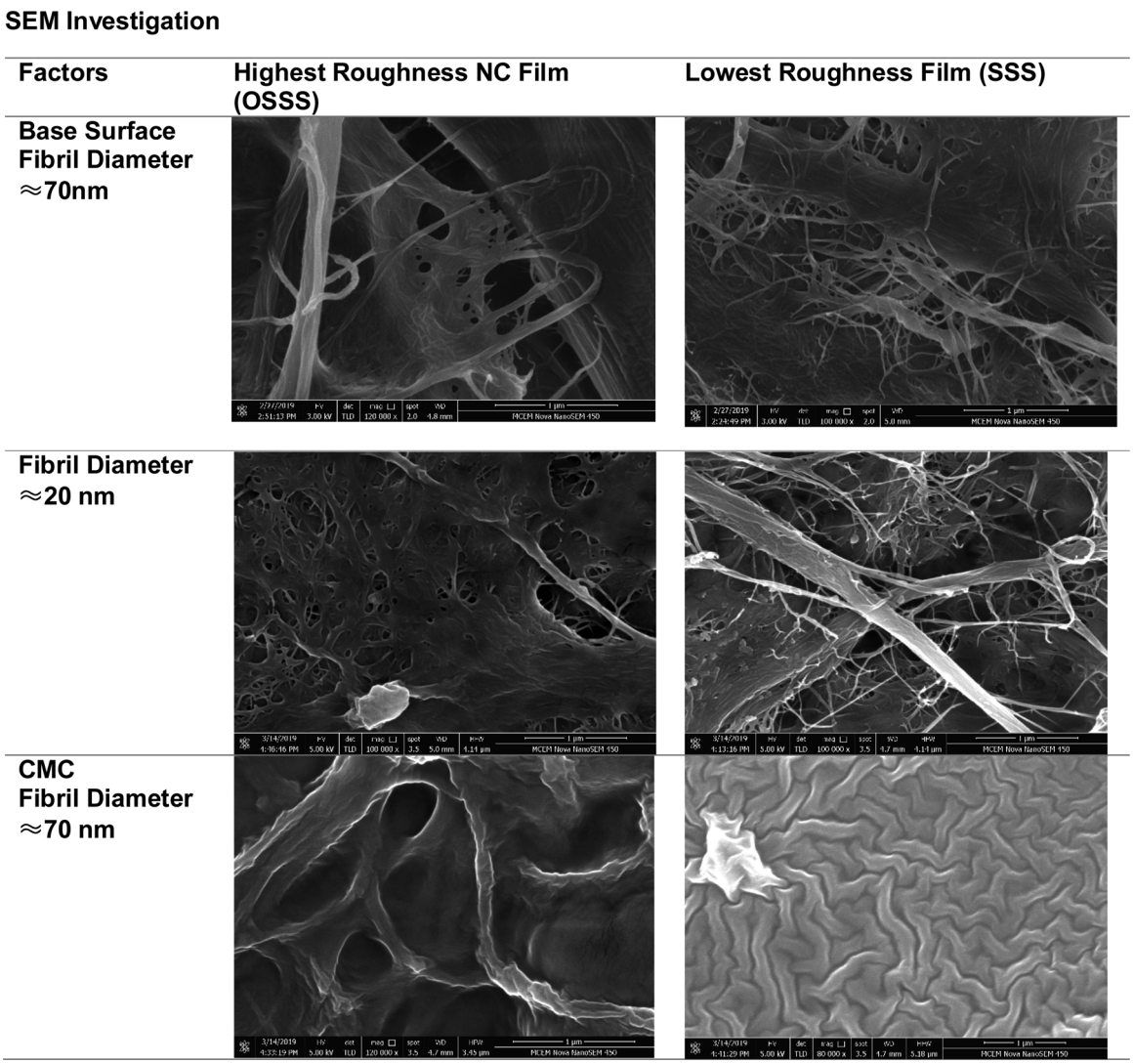

Fig. 3. SEM micrographs of smooth NC film via spraying.

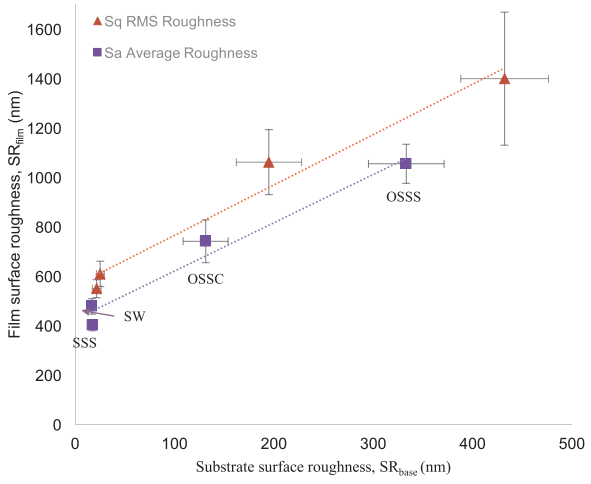

Fig. 4. Effect of the substrate surface roughness on the film surface roughness of the NC samples (Sa and Sq).

roughness decreases with the fibre diameter as the lines with smaller fibre diameter are below the untreated NC. That means that decreasing the fibre diameter decreases the roughness, but that the roughness is still modifiable by changing the substrate.

The controlling order of RMS roughness of NC films was CMC addition > substrate surface > fibril diameter and can be evidenced from the y-intercept of the line in the Figs. 6 and 7 decrease. The intercept for default NC, NC with one and two pass homogenization, CMC- Default NC film in Fig. 7 are evaluated to be 616.11 nm, 527.51 nm, 432.9 nm and 330.8 nm respectively.

The gradient of the linear trend line between RMS roughness of NC film and substrate surface decreased in the order of CMC addition > substrate surface > fibril diameter. The gradients are evaluated to be 1.95 for Default NC, 1.88 for NC from the 1 st homogenization, 2.05 for NC form 2nd homogenization and 0.41 for CMC-Default NC film.

The slope for CMC – Default NC film was lowest compared with the slope from base substrates and fibril diameter. The base substrates has a large influence on the roughness of NC film when there is no addition of CMC in the NC suspension.

Similarly, the effect of fibre diameter on the surface roughness of the NC film prepared from OSSS, SSS and SW was also investigated. The Y intercept in Fig. 9 decreases with the smoothness of the substrates. The Y- intercept for OSSS, SSS and SW are reported to be 1212.1 nm, 413.22 nm and 324.6 nm, respectively. This data concludes the effect of surface roughness of the substrates on the film with diameter distribution of fibrils in the order of OSSS > SSS > SW.

Fig. 9 shows that the effect of fibril diameter is much smaller than the effect of surface roughness, when no addition of CMC occurs. The

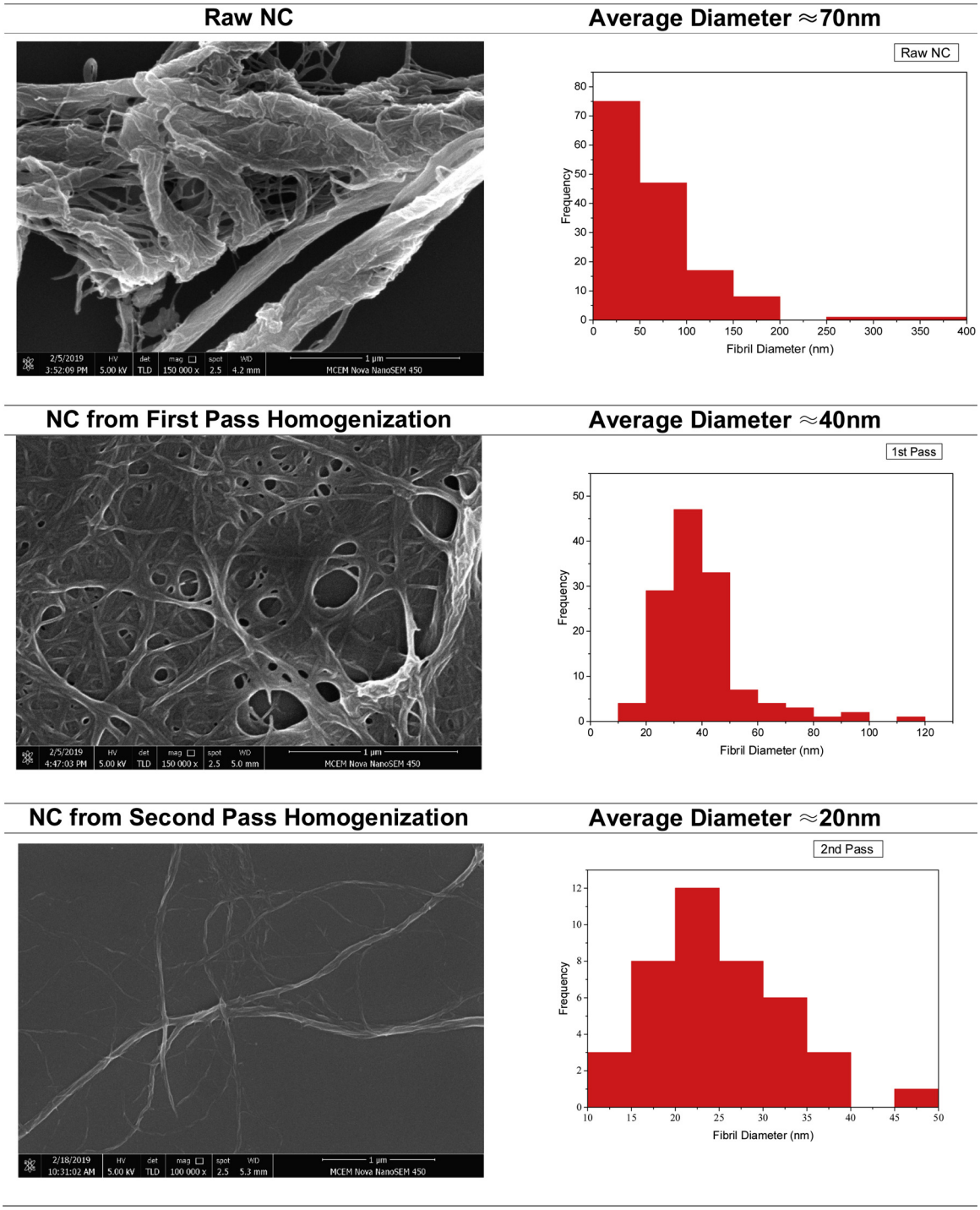

Fig. 5. SEM Micrographs of Raw NC and homogenized NC with fibril distribution.

CMC data has a different trend. That is with the CMC addition, there is little effect of surface roughness, meaning that at high levels of base surface roughness, CMC is much more important than fibre diameter. At very low levels of base surface roughness, the effects of CMC addition and fibre diameter reduction are much closer, with CMC having approximately double the effect of fibre diameter reduction.

The CMC results were very interesting. Both the slope and the intercept decreased when CMC was added with surface roughness which was much lower than the other three types of NC. The lower slope indicates that with the addition of CMC, the roughness becomes less dependent on the substrate roughness. Moreover, it will be worthwhile to investigate the addition of varying amounts of CMC and establish the minimum level of smoothness that is attainable using this method.

The plot between surface roughness of NC film and fibril diameter are shown in Figs. 7 and 8. The intercept and slope of the correlation depends on the fibre diameter and aspect ratio which both decreased with number of passes in the high-pressure homogenization. High pressure homogenization consumes significant energy for fibrillation of fibres and increases the viscosity of the NC suspension, which could cause clogging in a homogenizer. Additionally, the increased viscosity of NC suspension caused difficulties with spraying. Sometimes, the highly viscous NC suspension blocks the nozzle in the spray gun and results in poor spray jet of NC suspension. Adding carboxymethyl cellulose (CMC) to the unhomogenized NC suspension reduces fibre

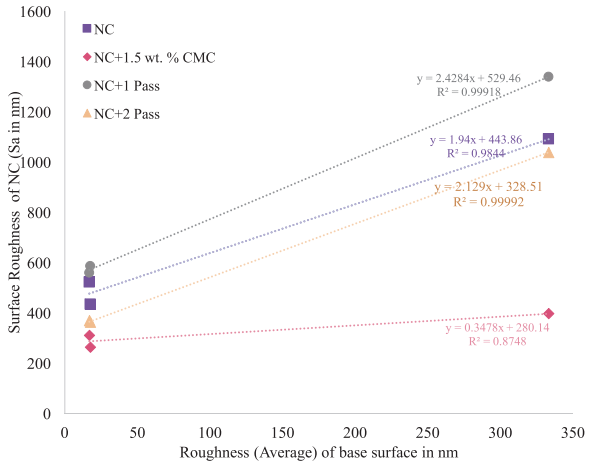

Fig. 6. Effect of homogenization and CMC addition in NC suspension on the surface roughness (Sa) of NC film.

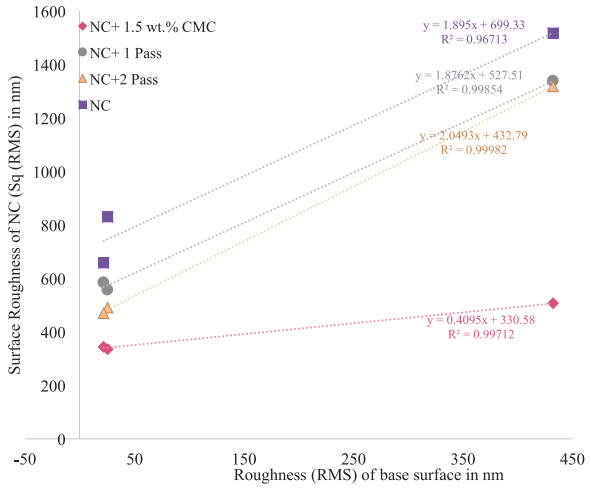

Fig. 7. Effect of Homogenization and CMC addition in NC suspension on the RMS surface roughness. Sq of NC film.

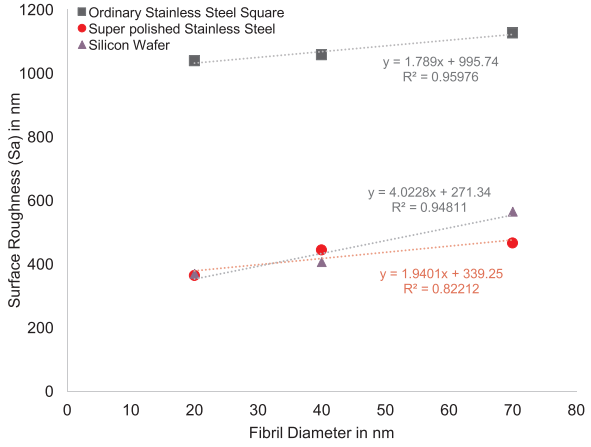

Fig. 8. Effect of fibril diameter of NC on roughness, Sa of NC film.

friction and enhances the smoothness of the film.

4. Discussion

Spraying is a rapid process to form the NC film and can retain part of the smoothness of the base substrate. It is a single step process and the

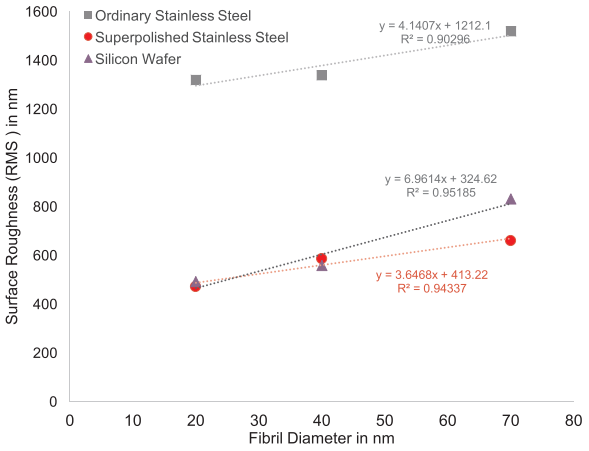

Fig. 9. Effect of fibril diameter of NC on RMS roughness, Sq of NC film.

spraying time is independent of NC suspension concentration. The parameters controlling the smoothness of NC film are surface roughness of base substrates, fibril diameter of NC and friction modifiers such as carboxymethyl cellulose (CMC). The RMS roughness, Sq, of the NC film via spraying on the steel substrates varied from 1400 nm to 550 nm and was reduced to 336 nm with a loading of 1.5 wt.% CMC in 1.75 wt.% NC. The lowest value is under the maximum surface roughness of cellulose nanofibre material required for electronic applications, which is in the range of 310 nm–470 nm [4]. This is comparable with the maximum surface roughness of plastic substrates, which is normally 400 nm, for fabricating electronic circuits. The smooth surface and texture of the base surface like plastic material can be also replicated on the nanocellulose film [19,20] produced via solvent casting method. However, both solvent casting and vacuum filtration method are time consuming process for NC film formation.

The surface roughness of NC film could be reduced by high pressure homogenization, which reduced the fibre diameter and length. When spraying on the SSS substrate, the RMS roughness was reduced from 550 to 470 nm after 2 passes through the homogenizer. However, beyond 2nd pass homogenization, the viscosity of the NC suspension increases and crosses the sprayable limits of the Wagner 117 professional spray system, causing nozzle blockage in the spray gun. High pressure homogenization is also an extremely energy intensive process. The base substrates such as polished stainless steel and silicon wafer are also quite expensive. The most interesting finding was the effect of CMC. When this was added to raw NC suspension to reduce fibre friction and surface roughness of the film, the Sa and Sq for CMC – NC film decreased from 396 ± 28 nm to 262 ± 26 nm, and 508 ± 34 nm to 345 ± 37 nm respectively, when spraying on ordinary stainless steel. This is very close to the range required for application as a plastic substrate for electronics.

The controlling order of roughness of NC film was CMC addition > substrate surface > fibril diameter. The reduction of roughness of NC film by CMC addition is more effective than that of base substrates and fibrillation of NC via high pressure homogenization. Adding CMC in Raw NC suspension makes the smoother film even when the suspension was sprayed on the rougher substrates. The effect of CMC addition is only reduced when spraying on highly smooth substrates such as polished stainless steel plates and silicon wafer.

The experimental data concludes that high pressure-homogenization of NC has at most a small effect of the surface roughness of the film. The data shows that fibril diameter has the least effect and that CMC by itself or substrate roughness by itself have significant effects, but that there are interactions. Thus substrate roughness is not important if using CMC and CMC addition only has a small effect if spraying onto a very smooth surface, such as silicon wafers. In neither case does fibril diameter have much of an effect.

The mechanism of replication of surface roughness from substrates to NC film remains obscure. Possibly, the mechanism can be explained with adhesion of fibrils and inter-fibre bonding with the substrate. Currently there are three different mechanisms proposed regarding the adhesion of cellulose fibres. Cellulose fibres have irregular surfaces and the interaction between the rough surfaces and interlocking of the fibres can produce adhesion. The interactions of the fibres and the base substrate is also influenced by the intermolecular diffusion of the cellulose chains and finally all of these components are controlled by force interactions. The interactions such as hydrogen bonding, van der Waals and electrostatic forces are important in cellulose fibres and can not only occur between the fibres and the substrate but also between the individual fibres themselves [21,22].

Mechanical interlocking of cellulose nanofibres with substrates would be a common mechanism of replication of roughness from ordinary stainless-steel plate containing many complex scratches and lines. Both the square and circular stainless-steel plates, were not even and their surfaces had significant asperities compared to the silicon wafer and super polished stainless-steel surface. These larger asperities imprinted on the NC films and produced rougher surfaces. Therefore, spray coated cellulose nanofibres were easier to peel from these surfaces. For the super polished stainless-steel surface, the height of asperities was much smaller and highly smooth surfaces were created due to the lack of large asperities. Super polished stainless-steel surface has an average Sa and Sq roughness of 17 nm and 22 nm, respectively and reflectivity of greater than 90 % The surface hydroxyl groups of cellulose nanofibres interacts well with the surface resulting in a smoother NC film.

The silicon wafer used also has an ultra-smooth hydrophilic surface having an average Sa and Sq roughness of 17 nm and 25 nm, respectively. The surface hydroxyl groups of the NC interact with silicon surface via chemical bonding such as hydrogen bonding, van der Waals and electrostatic forces. Due to the formation of hydrogen bonds among the cellulosic nanofibrils, the fibril surfaces are in contact with the base surface at a molecular level. The reported molecular distances varies from 0.15 to 0.35 nm [21,23,24]. These values are much smaller than the actual dimension of the surface roughness of fibres. Thus, the roughness can drastically limit the molecular contact between adjacent surfaces [25].

It is found that 1.5 wt. % CMC added into 1.75 wt.% NC suspension drastically reduced the surface roughness of NC film via spraying. CMC is a water soluble polysaccharide that could modify rheology of the NC suspension and by adsorbing onto the surface of NC [26] [27].

The NC suspension has strong inter-fibrillar interactions between cellulose nanofibrils and shows non-Newtonian thixotropic behaviour. It requires high shear force to decrease the viscosity of suspension. Due to this characteristic of NC, it could elevate the surface roughness of film via forming flocks or aggregates of fibrils in the film. Therefore, adding CMC into suspensions of NC reduces the friction between the surfaces of cellulose fibrils and enhances the dispersion of nanofibrils in the suspension [28–30]. The fibril interaction and friction in NC is reduced via ionic repulsion between nanofibrils resulting in good packing of the fibrils [31–33]. The ionic repulsion occurred between the carboxyl group of CMC and surface hydroxyl group of NC [34].

5. Conclusion

Highly smooth nanocellulose (NC) films were prepared via a one step process of spraying on impermeable substrates. Their smoothness can be engineered by simply changing the base surface roughness and part of its surface roughness is replicated on the NC film. Smoothness of the film was further increased via spraying of reduced NC fibril diameter suspension and also adding polymers into NC suspension. The parameters controlling the roughness of the NC film is in the order of carboxy methylcellulose (CMC) addition > base surface > fibril diameter. The effect of CMC concentration on the surface roughness of the film should be further investigated. The results confirm spraying as a rapid and one step process for engineering the surface roughness of NC film for commercial applications.

The spraying process could reduce the time for film formation from 10 min in vacuum filtration to ˜1 min in current practice. The roughness of the spray coated side of the NC film replicated from the base substrates and can be tailored through utilisation of various substrates, which is another advantage in this process. To conclude, spray coating process has a dual functionality of forming the film in a rapid manner as well as replicating part of the smoothness from the base substrates into the nanocellulose film. As we have reported, spray coating was able to handle high solid concentration of fibres to make the NC film. By this method, spraying process can handle CMC -NC with high solid concentration to make a highly smooth film, even when using relatively rough substrates.

CRediT authorship contribution statement

Kirubanandan Shanmugam: Conceptualization, Investigation, Formal analysis, Writing - original draft, Visualization. **Christine Browne:** Formal analysis, Writing - review & editing. **Gil Garnier:** Writing - review & editing, Supervision, Funding acquisition. **Warren Batchelor:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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